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Chemical thermodynamics and elements of structure in oxide melts

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Abstract. The data analysis has shown that various structural elements of an oxide melt influence on a concrete property of a system differently. It is interesting to extract the elements with dominating influence on each property and elements with the negligible effect. We show that monomers SiO_4^{4-} and ring structures $Si_4O_{12}^{8-}$ do not influence neither on density, nor on the surface tension of the PbO-SiO_2 system.

1. Introduction

The physicochemical properties of disordered condensed substances, in particular, polymeric silicate melts are determined by their structure. The basic structural units are silicate-oxygen anions of a various degree of complexities, which are in a chemical balance between themselves and "free" ions of oxygen. Complex anions represent repeating parts of the silicate-oxygen tetrahedron, formed as a result of polymerization reaction with the participation of monomers.

2. Elements of theory

Each structural component of a melt in the MeO-SiO_2 system has been estimated numerically depending on the number of monomers and its charge using Randič's χ-criterion [1] which was calculated as

$$\chi = \sum 1/(\nu_i \cdot \nu_j)^{1/2}, \quad (1)$$

Here ν_i and ν_j are the numbers of bonds originating at a given and neighboring graph vertices, and summation is performed over all bonds connecting the vertices.

The standard Gibbs energies of formation of molten silicates, borates, phosphates, titanates, aluminates and ferrites from corresponding undercooled liquid oxides (ΔG_{sl}^0) at the temperatures of fusion of the compounds were calculated basing on the assumption that the heat capacities of solid and undercooled liquid oxides are equal to each other [2]. The values for ΔG_T^0 were determined using the Temkin-Shvartsman's method and our results.

The interaction of complexes leads to complication of their structure and is accompanied by the injection of "free" oxygen anions into the melt:

$$Si_nO_{3n+1}^{2(n+1)-} + SiO_4^{4-} = Si_{n+1}O_{3n+4}^{2(n+2)} + O^{2-}. \quad (2)$$

The electrical charges of the complex anions and "free" oxygen anions are indemnified by the positive charge of metallic ions. On the basis of the stated theoretical positions a quantitative scale of the short-range order structure elements in oxide melts has been developed [3] and connected with the standard Gibbs formation energies. Further, as a first approximation, we have limited ourselves only by those structural elements, which have been revealed early in the binary systems in independent researches using the trimethylsilylation method [4].

Therefore, we include into our analysis "free" oxygen - O^{2-}, monomers – SiO_4^{4-}, chains- $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$ and rings - $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$, $Si_6O_{18}^{12-}$. The larger formations are designated as $(SiO_2)_i$. Bridge - O^0 and non-bridge - O^- oxygen ions also correspond to their own values (Table 1).

The dependence of any physicochemical property, for example, density or surface tension, on concentration at certain temperature and pressure is determined by another numerical sequence. Thus, the task of revealing of correlations between properties and parameters of structure is reduced to determination of coefficients describing contribution of each structural element into a chosen property. This task was solved by a method of multiple regressions taking into account all structural elements presenting in the melt of a given concentration.

Table 1. The quantitative parameters of anion elements in a disorder oxide melt.

n^a or m^b	$\chi_{O^{m-}}$	$\chi_{Si_nO_{3n+1}^{2(n+1)-}}$ $(n+1)/\sqrt{1.5}+(n-1)/\sqrt{2}$ at n>=1	$\chi_{Si_nO_{3n}^{2n-}}$ χ_n at n>=3
0	0.075	-	-
1	0.092	1.633	-
2	0.109	3.157	-
3	-	4.680	4.571
4	-	6.020	6.094
5	-	7.727	7.618
6	-	9.252	9.142

[a] *n*- number of tetrahedrons in a chain or a ring
[b] *m* - charge of anion

It is known, that SiO_2 melt is completely polymerized and represents spatial grid of tetrahedral SiO_4, connected through the oxygen bridges. In the binary PbO(CaO)-SiO_2 systems in an interval of SiO_2 concentrations up to 33 wt. % there are mainly monomers, "free" ions of oxygen O^{2-} and metal cations $Pb^{2+}(Ca^{2+})$. In the melt of a pure metallic oxide only anions of "free" oxygen and $Pb^{2+}(Ca^{2+})$ cations are available Thus, structural elements existing in the system at three concentrations are known.

The experiment does not allow revealing of contribution of a concrete structural unit to a certain property of the system (for example, density). Hence, to find coefficients of linear regression it is necessary to use additional information concerning to the distribution of structural units in melts of various concentrations. This problem was solved using the opportunities of the polymeric models [5, 6].

Let us designate the size of *i*-th fragment of a structure (Fr_i) as

$$Fr_i = C_i \lg(\chi_i), \tag{3}$$

where C_i is its concentration for the melt of a certain composition. Having two data sets, first of which is concentration dependence of a property sensitive to the melt structure, and the second are the corresponding fragment sizes, we have connected them as follows:

$$\lg(1/Y_j) = K_{0j} + \sum_{i=1}^{l} K_{ij} Fr_{ij}, \tag{4}$$

in which Y_j are values of the property and Fr_{ij} are the fragment sizes (Table 2) with the appropriate weight coefficients K_{ij}, l is the number of basic structural elements.

In this equation we have to determine factors K_{ij} and K_{0j}. In order to find them, we have to write down a system of the equations connecting concentration dependences of the property and the size of structural elements:

$$\begin{aligned} &\lg(1/Y_1) = K_{01} + \sum_{i=1}^{l} K_{i1} Fr_{i1} , \\ &\text{- - - - - - - - - - - - - - - - - - -} \\ &\lg(1/Y_p) = K_{0p} + \sum_{i=1}^{l} K_{ip} Fr_{ip} , \end{aligned} \qquad (5)$$

where p is a number of equations in the system.

Having calculated coefficients of the regression, one can estimate the contribution of each fragment to the property of system comparing their values.

3. **Results of calculation**

This approach was used in our study of silicate systems. In particular, concentration dependences of density and surface tension of the systems $PbO\text{-}SiO_2$ at 1273 K and $CaO\text{-}SiO_2$ at 1973 K are available [7]. Using distribution of the structure elements we have chosen 10 points with a concentration step of 0.1 (in molar fraction of SiO_2) and have constructed the system of equations (5), in which the right part takes into account the influence of the melt concentration on a size of various structural units, and the left one – the concentration dependence of the property.

Let us note, that the distribution of non-bridge, bridge and "free" oxygen and silicate anions were taken into account separately, without joining of these concentration dependences in one equation. As a result, we have got twenty equations (p), each containing twelve unknown values, eleven (l) of which are the coefficients of the basic structural fragments (K_{ij}) and free member of the equation (K_{0j}). The decision of the redundant system of equations was carried out under condition $p > l+1$ with the advanced algorithm [8] by the method of least squares.

The results of our calculation for the $PbO\text{-}SiO_2$ and $CaO\text{-}SiO_2$ systems are given in table 2 and the concentration dependences of density for the $PbO\text{-}SiO_2$ system are represented in Figure 1.

Table 2. Coefficients of the linear regression.

Element of structure	i	$\lg \chi_i$	$K_i(\rho)$ $PbO\text{-}SiO_2$	K_i(V) $PbO\text{-}SiO_2$	$K_i(\sigma)$ $PbO\text{-}SiO_2$	$K_i(\rho)$ $CaO\text{-}SiO_2$	K_i(V) $CaO\text{-}SiO_2$
----	0	–	-3.664	4.931	-2.405	-3.391	1.601
O^0	1	-1.036	-0.009	0.136	-	-0.013	-
O^-	2	-1.125	0.080	-	-0.043	0.053	-0.094
O^{2-}	3	-0.963	0.043	-0.343	-0.138	-1.012	1.664
SiO_4^{4-}	4	0.213	-0.721	-1.344	-	-0.560	0.682
$Si_2O_7^{6-}$	5	0.499	1.197	1.476	-0.528	0.421	-
$Si_3O_{10}^{8-}$	6	0.670	-2.320	-	1.932	-0.554	-
$Si_3O_9^{6-}$	7	0.660	-	-2.014	-	-	0.413
$Si_4O_{12}^{8-}$	8	0.785	-	-	-	-	-
$Si_6O_{18}^{12-}$	9	0.882	-	-	-	-	-
$(SiO_2)_i$	10	0.905	-	-0.134	-	-	0.076
Me^{2+}	11	-0.050	3.113	16.290	-3.314	0.840	-0.677

It can be seen that some values of the *Kij* factors are absent in Table 2. The reason is: in initial approximation all weight coefficients were taken into account, however, at subsequent calculation some of them were found to be insufficient.

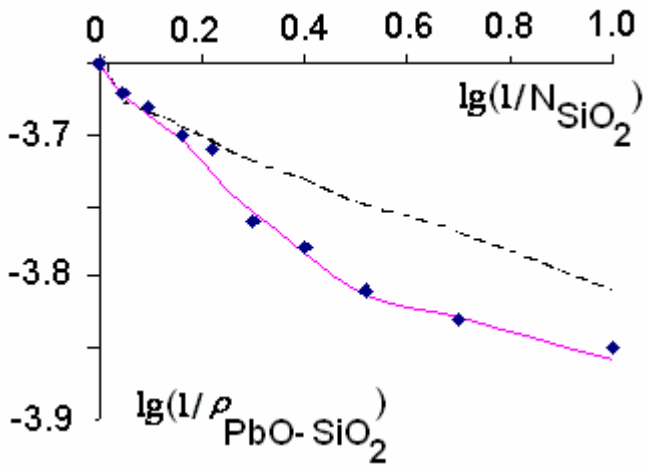

Figure 1. The concentration dependence of density in the PbO-SiO_2 system: points are the experimental data [7]; continuous line is a result of the calculation; dashed line is the result of the same calculation without taking all forms of oxygen into account.

4. Discussion

So, the approach using before in organic chemistry was applied for determination of the influence of various structural elements of a high polymerized melt on their selective activity and, as a result, for revealing correlation dependencies "structure-property" in the PbO (CaO)-SiO_2 systems.

At the present time the polymeric model does not allow estimation the difference of concentrations of the structural elements in the surface layer and in volume. Therefore, while our analysis of contribution of various structural elements in the surface tension and density we took into account the changes in their concentration in the volume only. It can be a reason of some discrepancy of the measured and calculated property values.

Thus, it was shown that proposed method of the linear equation of multifactor regression allows combination of two sets of property values (density ρ, molar volume V, surface tension σ) of a melts and its structure. Similarly, it becomes possible to describe some other physical or physicochemical properties, such as conductivity, viscosity etc., and as well to expand this approach to multi component systems containing complex structural elements.

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